

Pre-Proposal

Remediation of Cr(VI) in the Vadose Zone of Hanford Site 100 Areas

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Chromate was used throughout the 100 Areas (100 B, 100 C, 100 D/DR, 100 F, 100 H 100 K) as a corrosion inhibitor in reactor cooling water at concentrations between 2.0 and 0.7 mgL⁻¹. After passing through the reactor, cooling water was transported through large-diameter underground pipes to retention basins for thermal and radioactive cooling prior to release to the Columbia River. In the 100-D Area, chromate concentration at >4000 µg/L have been measured in the groundwater, which demonstrates that the source of chromate is not the cooling water but a more concentrated source. In addition, chromate concentrations up gradient of the in situ redox manipulation (ISRM) barrier have remained high since the plume was discovered in 1999, suggesting that there is a chromate source associated with the vadose zone.

Currently EM-22 has funded two Cr projects designed to (1) better delineate the 100-D Area groundwater plume and possibly identify potential vadose zone Cr(VI) sources, and (2) characterize vadose zone chromate and its geochemistry. While these projects' success will address important issues of spatial and chemical distribution of Cr(VI) in the vadose zone, there remain issues regarding remediation of Cr contaminated vadose zone sites. In general there are two remediation strategies that are currently being considered, which assume that the Cr(VI) sources are beyond the depth reasonable for excavation and burial, and are based on the reduction of Cr(VI) to an insoluble Cr(III) form (generally Cr(III) hydroxide):

1. Cr(VI) reduction to Cr(III) in situ by H₂S_(g) (in situ gaseous reduction [ISGR])
2. liquid Ca-polysulfide_(aq) injection.

The clear distinction between the two strategies is that the gas reductant would limit the transport of Cr(VI) out of the vadose zone, while the potential from Cr(VI) transport ahead of the Ca-polysulfide reductive front will occur with a liquid reductant injection. While both techniques could be effective, their efficacy will depend on the Cr(VI) spatial distribution (extent of contamination) and its physical-chemical form. The latter issue is the focus of this preproposal.

The Hanford formation sediments seem ideal for the use of in situ reduction of Cr(VI) due to the coarse-grained nature of the sediments. However, the scientific basis for ISGR treatment of vadose zone Cr(VI) have not dealt with Hanford formation sediment contaminated with the high Cr(VI) concentrations suspected or observed in the 100-D Area (recent excavation of a subsurface pipeline) or those excavated/identified recently in the 100-B/C area (confirmed concentrations in excess of 3500 mg/kg and possibly in the % range [$> 10,000$ mg/kg]). Large concentrations such as those expected in the vadose zone could affect the efficiency of ISGR. Similarly, the age of these contaminated sediments marginalize the efficiency of a Ca-polysulfide injection or ISGR because of Cr(VI) physical/chemical form. Issues confronting the use of either reductant are:

1. The mass of reductant required to reduce the Cr(VI) and other electron acceptors in the sediment and the kinetic relationships between the mass flow rate of the treatment agent and Cr(VI) reduction

2. Isolation of a substantial percentage of Cr(VI) in small pores (transport limited) or as only slightly soluble solid phases (e.g., BaCrO_4 or co-precipitated with calcium carbonate)
3. Cr(VI) in small pores effectively occluded from reductant as Cr reduction proceeds - precipitation of reduced Cr species within the pore space connectivities traps Cr(VI) within pores
4. Transport of Cr(VI) ahead of Ca-polysulfide front

These issues directly relate to the efficiency of reduction, the potential for residual Cr(VI) pools after remedial action, and the potential for leaching Cr(VI) to groundwater.

To address these issues, we propose linking a series of laboratory flow studies with the currently funded Vadose Zone Chromium Characterization and Geochemistry Project. While the current project is designed to characterize the Cr(VI) geochemistry and leaching in these sediments, a corollary study using the same materials could be performed to investigate the efficacy of the two reductants as a remediation tool for potential vadose zone Cr sources. Using the same materials in both studies would maximize sediment characterization data currently being performed, focus post-mortem reductant exposed column sediment examination, and minimize time and expense of future remediation studies of vadose zone Cr(VI).

The proposed studies foci will be on addressing the aforementioned issues of Cr(VI) reduction in vadose zone sediments.

- Studies of ISGR by $\text{H}_2\text{S}_{(\text{g})}$ will use two to three column tests at previously utilized gas concentrations (200 ppm) to determine (1) H_2S breakthrough, (2) effect of water vapor saturation/ O_2 scrubbing (using $\text{N}_{2(\text{g})}$) on Cr(VI) reduction efficiency, and (3) impact of Cr(VI) form on reduction. The latter issue would be resolved through the use of freshly contaminated sediments (perhaps from the 100-D pipe breach) and sediments that have been contaminated for >40 yrs (sediments identified in the 100-B/C Area). By using the same sediments characterized as part of the chromium characterization project and monitoring out gassing of columns and post-reaction dissection chemical analysis, the aforementioned issues will be addressed.
- Studies of Ca-polysulfide Cr(VI) reduction will follow a similar approach utilizing currently applied concentrations (~ 10% to 20% solutions) and scaled flow velocities to determine 1) Ca-polysulfide breakthrough, 2) Cr(VI) mobilization, and 3) the effectiveness of Ca-polysulfide on reduction rate of low solubility Cr(VI) phases (e.g., BaCrO_4). Similar to the ISGR studies careful pre- and post-reaction analysis data will be used to address issues of interest.

The importance of the pre-reaction characterization cannot be emphasized enough. Knowing, prior to the reductant studies, the chemical and physical distribution of Cr(VI) in sediment will save substantial funds, time, and limit the breadth of post-reaction column sediment analysis necessary to characterize the efficiency of the reduction process. Further, these analyses will directly relate the impact of Cr(VI) aging in the vadose zone to the effectiveness of both proposed reductants.

Estimated Cost/time: \$225K, 12 to 14 months - perform studies, post-reaction sediment analysis and data analysis